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INHIBITION OF HYDROGEN ABSORPTION DURING PLATING OF HIGH STRENGTH STEELS

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JULY 1984

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Hydrogen absorbed by steel parts during the cadmium plating process can cause cracking failures in service. This feasibility study was concerned with the effects of precoating steel with an electroactive coating on the amount of hydrogen absorbed during subsequent cadmium plating. Redox couples having rather negative standard redox potentials were successfully immobilized on steel surfaces. However, these coatings either had no effect or increased the amount of hydrogen absorbed during the cadmium plating step. Possible reasons for this behavior are given in this report along with other pertinent

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experimental findings. Alternate approaches to solving the hydrogen
absorption problem are discussed.

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SECTION 1
INTRODUCTION AND SUMMARY

This final report gives the results of a feasibility study performed by SumX Corporation for the Naval Air Development Center (Contract Number N62269-83-M-3349). The purpose of the research was to determine the effect of coating steels with electroactive coatings on the hydrogen absorption properties of the steel during subsequent plating with cadmium. High strength steels used in a marine environment are usually cadmium plated for corrosion protection. Hydrogen is evolved during cadmium plating from aqueous solutions, and some of the hydrogen is absorbed by the cadmium plate. The absorbed hydrogen can then diffuse into the steel where it may cause failure of stressed parts.

A recent development in electrochemistry has been the use of surface immobilized redox couples to modify the redox behavior of metals. We have been investigating the application of chemically modified electrode methods to corrosion protection of active and active/passive metals [1]. If such a surface immobilized redox couple could decrease hydrogen absorption during plating, it could significantly decrease the danger of hydrogen embrittlement and thereby decrease the need for a post-plating bake cycle to remove hydrogen from plated parts, a procedure which has limited effectiveness.

A number of preliminary tests were made in this program to select redox couples and coatings for testing this possibility. Negative standard potential couples and the materials used to bind them to the steel membrane were tested and the most promising were selected for testing in a two compartment plating/hydrogen diffusion cell. Hydrogen diffusion data were then obtained during and after cadmium plating, both with or without the surface redox couple. No significant improvement in the amount hydrogen absorbed or the rate of its diffusion from the cadmium plate into the steel was found when any of the candidate electroactive

coatings was applied to the steel substrate prior to electroplating.
Attempts to prepare a positive standard potential redox couple on steel
failed due to gross corrosion or instability of the immobilized couple.

The last experiments performed in this feasibility study used
an alternate hydrogen measurement system called a barnacle cell.
Results again showed no measurable effect due to coating with redox
couple. However, the barnacle cell gave results more rapidly and with
apparently better precision than the usual two compartment cell.

The plating/hydrogen diffusion results indicate that the
majority of absorbed hydrogen is initially present in the cadmium plate,
and that this hydrogen will slowly diffuse into the steel substrate. It
appears that a thin interposed coating could at best delay the rate of
hydrogen transfer. Since the majority of hydrogen is present initially
in the cadmium plate, it would seem that only changes in plating proce-
dures can hope to significantly alter the total amount of hydrogen
absorbed. A complete solution to the hydrogen embrittlement problem
would require cadmium plating from a medium devoid of active hydrogen or
elimination of hydrogen formation by some other means.

SECTION 2

EXPERIMENTAL

Cyclic voltammetric tests were made in a standard three compartment electrochemical cell using either a Princeton Applied Research Model 363 potentiostat or a potentiostat built at SumX. Sweep rates were controlled by a Wavetek Model 185 function generator, and voltages and currents were recorded on a Houston Instruments Model 200 XY recorder.

Hydrogen permeation experiments were made in a two compartment cell similar to that used by Devanathan and Stachurski [2]. A thin steel membrane, generally 0.003 inch thick, separated the active and passive sides. Total steel electrode surface area was 20.5 cm^2 on each side. Hydrogen permeating to the side opposite that being plated was oxidized by the current flowing through a 100 ohm resistor driven by a PbO_2 electrode. Voltage across the resistor was recorded versus time on a Soltec Model 1242 strip chart recorder. Most plating experiments were performed using the potentiostat as a constant current source. In some experiments we used a long Luggin capillary ending within a few millimeters of the steel membrane. A SCE was then used to measure or control the steel potential during plating or hydrogen generation. The cell opening used for the Luggin capillary was closed when not used. The generating side of the cell also had a U shaped arm which was normally closed. This arm was used with a platinum auxiliary electrode during those experiments where hydrogen was generated from a NaF solution. The U shape presents the oxygen generated from reaching the steel membrane or mixing with the hydrogen. In such experiments the cell opening normally used for the cadmium electrode was closed. This equipment is shown in Figure 1.

Barnacle Cell: A barnacle cell similar in principle to that used by DeLuccia and Berman [3] was made from a 0.25 inch schedule 40
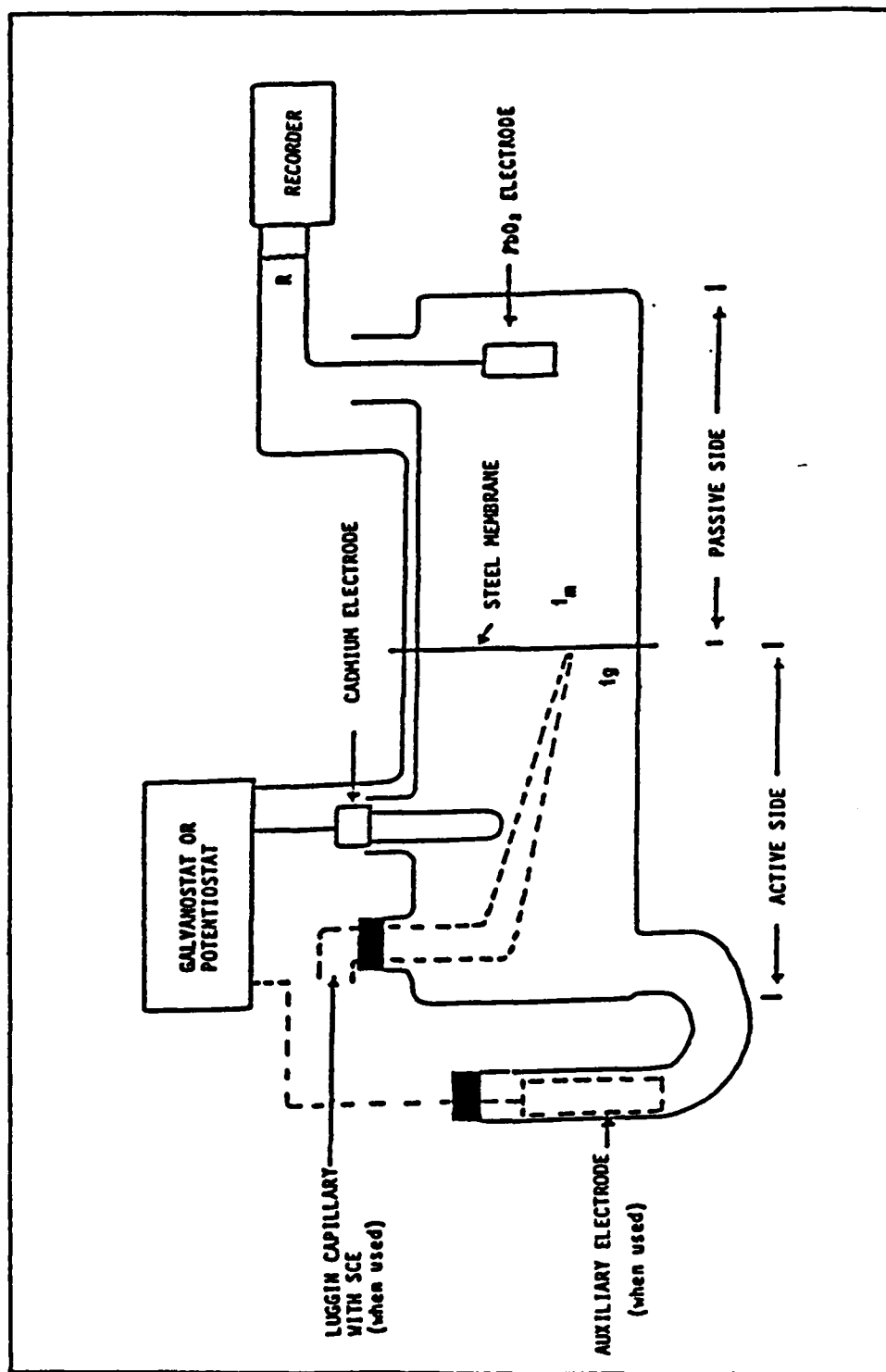
Figure 1. Two-compartment cell for hydrogen permeation studies.

PVC pipe el. One end of the el was cut off flush and a soft rubber gasket was inserted in the resulting shallow recess. When clamped to the steel specimen with a standard "three finger" clamp, an excellent seal resulted. A PbO_2 on 430 stainless steel electrode was connected to the steel specimen through a 1 K ohm resistor. The area exposed to 2 M NaOH was 2.0 cm^2. This cell is shown in Figure 2.

PbO_2 Electrode Preparation: A strip of 430 stainless steel, 0.5 inch by three inches was prepared by sanding with 320 grit SiC paper and degreasing. The stainless steel was immersed in 1.0 M $PbNO_3$, and 0.3 M $CuSO_4$; PbO_2 was deposited anodically at 2.5 mA/cm^2 for three minutes. The resulting $\alpha-PbO_2$ is reddish in color. In use, t' electrode is immersed to a level such that the uncoated steel is r exposed to electrolyte, which was 2 M NaOH.

Plating Solution: The cadmium plating solution used was prepared by dissolving 3.5 gram NaOH and 18.5 grams sodium cyanide in 250 mL water. Reagent grade cadmium oxide, 6.0 g, was then dissolved in the cyanide solution. In some experiments, 1 percent of the commercial "brightener" Udylite® 53 was added.

Nafion® Solution: One gram of Nafion 117 polymeric cation exchange film was placed in 50 mL ethanol and 50 mL water in a high pressure stainless steel reactor, sealed under nitrogen and heated to 230°C for two days. The resulting 1 percent solution was used directly or mixed with cationic redox couple. Nafion is a perfluorinated polysulfonic acid. The 1100 e.w. Nafion is not water soluble.

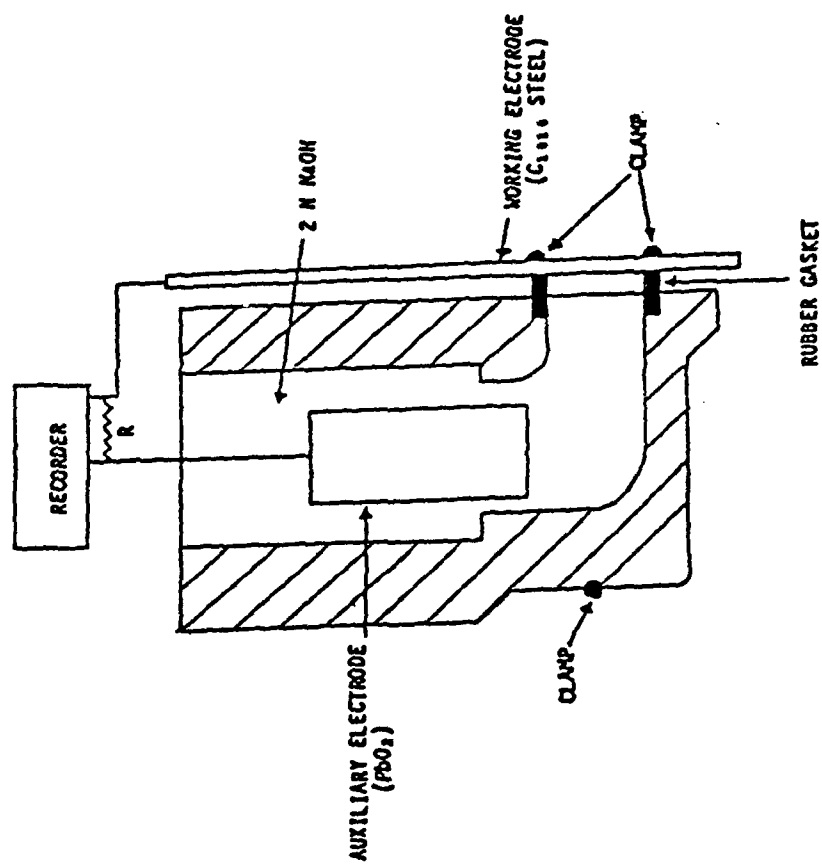Udylite®; Oxy Metal Industries

Nafion®; E I duPont

Figure 2. Barnacle cell for hydrogen permeation studies

Octylviologen: Octylviologen was prepared using the Menschutkin reaction [4]. 4,4'-dipyridyl (0.906 grams) was dissolved in 10 mL ethanol, 5.0 grams of 1-bromooctane were added and the mixture sealed under N_2 and reacted at 60°C for two days. The resulting solution was poured into 150 mL ether. Yellow crystalline octylviologen (1.6 g) was recovered by filtration.

Quaternarized Polyvinylpyridine: This polymeric anion exchange polymer was prepared using the Menschutkin reaction, following a simplified procedure similar to that of Braun, et al [5]. Commerical polyvinylpyridine (Reilly, 1.0 g) was dissolved in 10 mL ethanol, 0.6 grams 1-bromo-octane was added and the mixture was sealed under N_2 and reacted at 80°C for three days. The alcohol solution was poured into 150 mL of ether and 0.69 g of hygroscopic, water insoluble viscous oil product was recovered.

Prussian Blue: Prussian blue was deposited cathodically at 100 $\mu A/cm^2$ for 10 to 60 seconds from a solution of $FeCl_3$ (0.02 M) and $K_3Fe(CN)_6$ (0.02 M). Substrates for Prussian Blue coating were either bare metal or Nafion coated.

Methyl Viologen/Nafion: A 1 percent w/v solution of methyl viologen in 50 percent v/v ethanol in water was mixed with an equal volume of 1 percent w/v Nafion in 50 percent v/v ethanol in water. The mixture of methyl viologen and Nafion was coated on electrodes by painting with 1 drop per 3 cm^2, allowing excess to drain and then vacuum drying. Coverage was about 0.1 mg/cm^2.

Quaternarized Polyvinyl Pyridine/Anthraquinone Sulfonate: A 1 percent solution of quaternarized polyvinylpyridine in ethanol was painted on the electrode surface and vacuum dried. The electrode was then soaked in a 1 percent w/v aqueous solution of sodium anthraquinone-2-sulfonate.

Colloidal Platinum in Nafion: Prepared following the proce-
dure of Hirai, Nakao and Toshima [6]. Commercial polyvinyl alcohol
(150 mg) was dissolved in 25 mL H_2O. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$,
17 mg) was dissolved in the PVA solution and diluted with 25 mL ethanol.
Refluxing for 2 hours resulted in reduction of platinum to colloidal
metal. This was mixed in equal portions with Nafion solution for sur-
face application.

The following procedure was used in all experiments using the
two compartment hydrogen diffusion apparatus. The steel membrane was
prepared with any desired surface treatment and the treated side was
cemented to a teflon gasket with a quick setting epoxy adhesive. During
the last few minutes of the setting time of the epoxy, the steel mem-
brane with its glued-on gasket was assembled in the diffusion cell with
an additional teflon gasket on the passive, hydrogen oxidation side.
The oxidation side was then filled with 2 M NaOH, a PbO_2 electrode was
placed in the NaOH and then shorted to the steel. No recording was made
of the initial current, which includes both oxidation of hydrogen in the
steel and passivation of the steel surface. After being shorted to the
steel over night, the PbO_2 electrode was then reconnected through one
hundred ohm resistor at the recorder. Background current was generally
0.02 to 0.05 $\mu A/cm^2$.

The solution to be used in the plating (for hydrogen genera-
tion) side was then added. Any increase in background current was
generally associated with a leak on the generation side and concomitant
crevice corrosion. If the leak could not be corrected by tightening the
cell bolts—thus bringing the background oxidation current back down to
its value before addition of electrolyte, the cell was emptied,
dissassembled and a new membrane prepared.

If there was no increase in hydrogen oxidation current after
adding the electrolyte to the plating side, the plating or hydrogen

generation experiment was run. The hydrogen oxidation recording was
started several minutes before the experiment and allowed to run through
the experimental period and afterwords until the hydrogen oxidation rate
fell back close to the initial value. The integral of time·current was
calculated, beginning with the initial rise to the final time at which
the current was back close to the pre-experiment value. Steel membranes
were degreased and used without polishing unless otherwise noted.

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SECTION 3
RESULTS AND DISCUSSION

The approach taken in this research effort was to first determine which redox couples to use, then how to best immobilize them on the steel surface, and finally to determine the effect of the immobilized redox couple on the amount of hydrogen absorbed during electroplating with cadmium.

3.1   Cyclic Voltammetric Tests of Redox Couples

Cyclic voltammetry is an experimental electrochemical technique in which the potential of an electrode is swept back and forth through a voltage range of interest while the voltage and resulting currents are recorded. The resulting curve, "CV curve" contains information on the number of oxidation and reduction reactions, the potentials at which the reactions occur, reversibility of the reactions, and amounts (charge) of redox couple available for oxidation and reduction. Varying the rate of voltage change can yield information on kinetics and on diffusion processes involving the electroactive materials. Continuing the cyclic scans with the same electrode for an extended time gives information on long-term stability.

Redox couples were selected for testing on the basis of their known stability, reversibility and redox potential. Cyclic voltammetric curves for the materials used in this study are shown in Figure 3 through Figure 6. The E°'s ranged from - 0.62 volts vs SCE for methyl viologen to + 0.20 volts for Prussian Blue.

Methyl viologen, octylviologen and anthraquinone-2-sulfonate are water soluble materials. The method chosen to immobilize them was to utilize a water insoluble ion-exchange film. The redox couple was
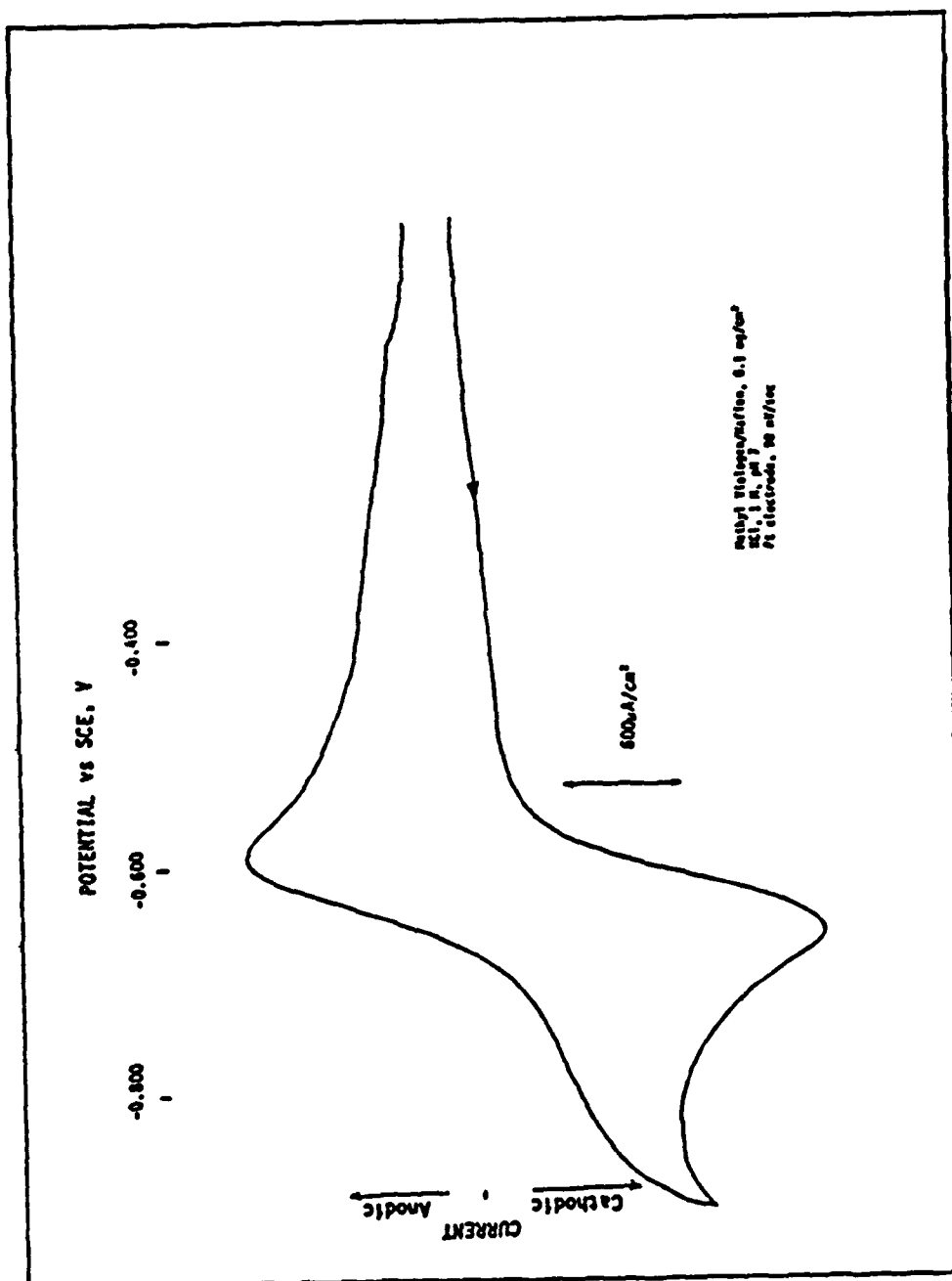
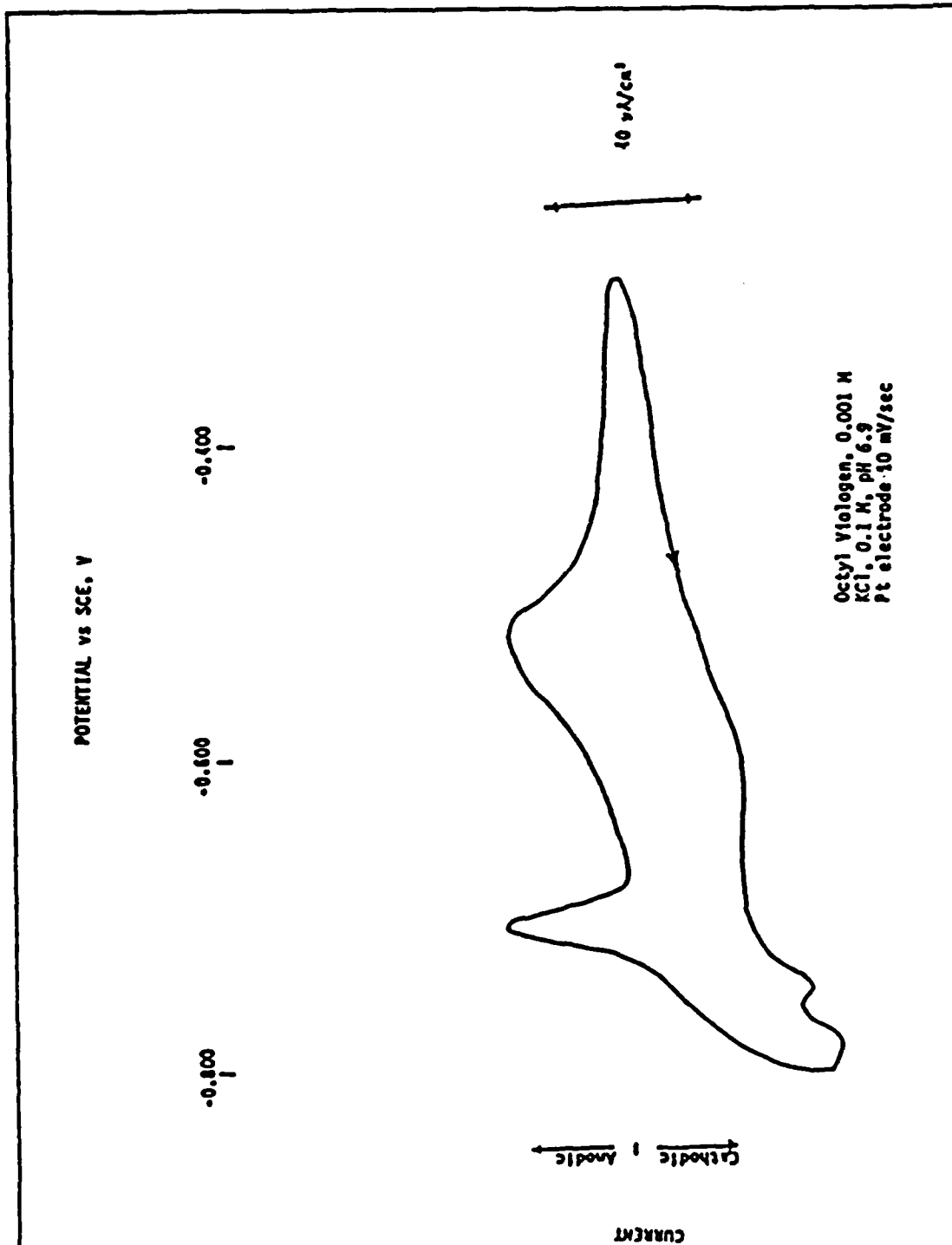Figure 3. CV curve for methyl viologen.

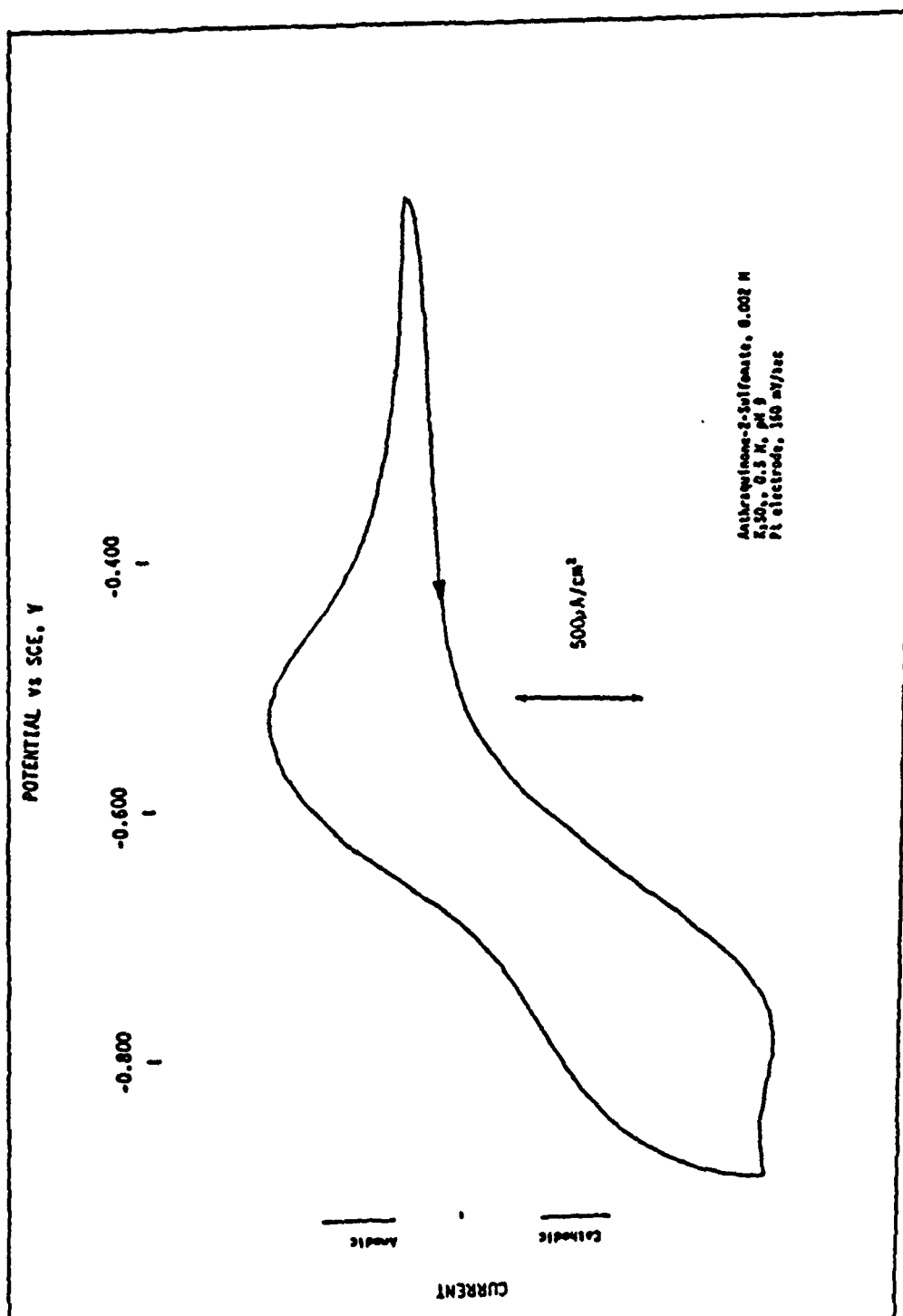Figure 4. CV curve for octylviologen.

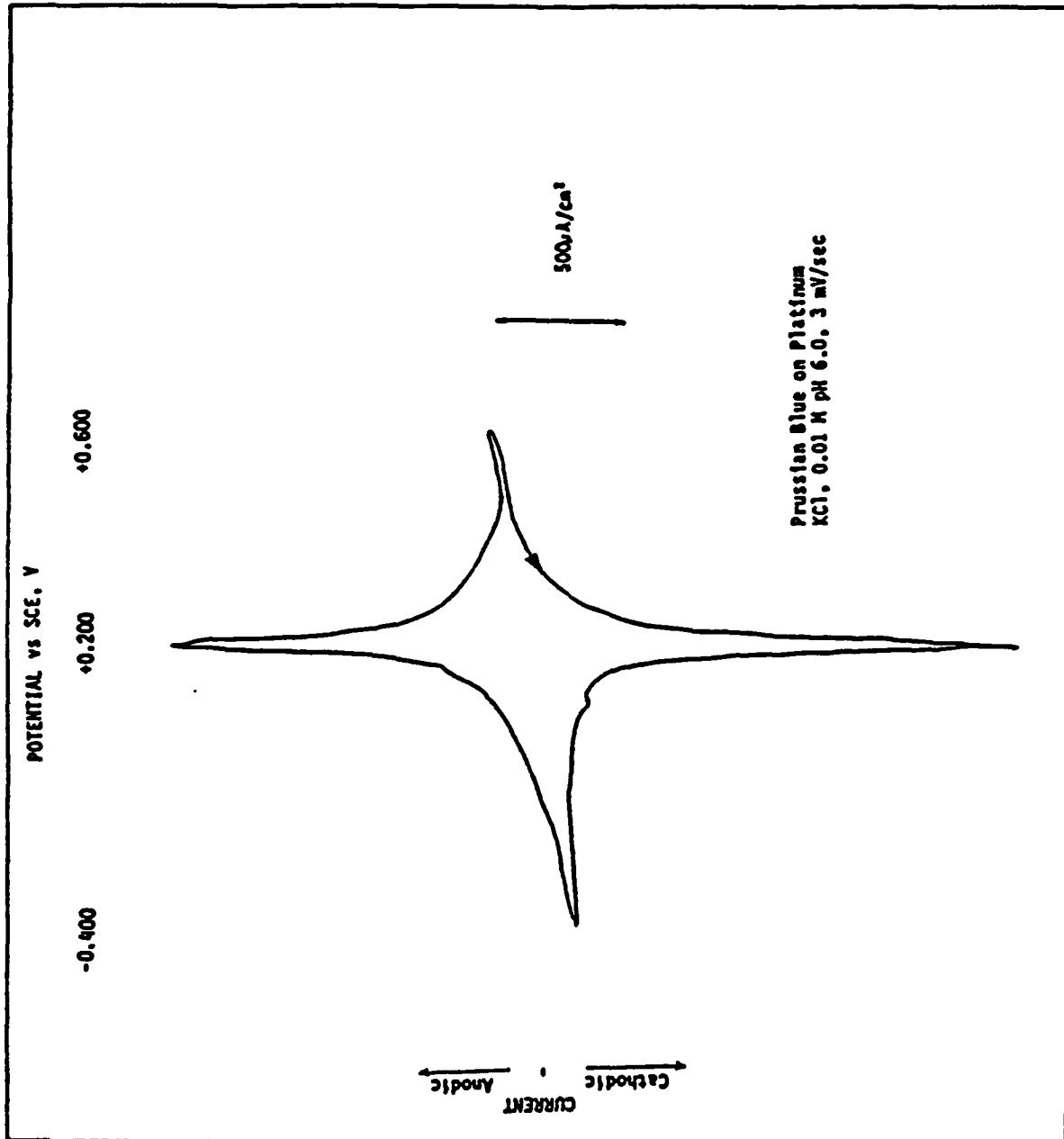Figure 5. CV curve for anthraquinone-2-sulfonate.

Figure 6. CV curve for Prussian Blue

either premixed with the ion exchange film or absorbed into the film after the electrode was coated with the ion exchange polymer.

Methyl viologen and Nafion were each prepared as one percent solutions in 50 percent ethanol/water. Equal volumes of those solutions were mixed and painted on the electrode surface. The resulting films were very thin, generally with coverage of about 0.1 mg/cm^2, and did not evenly cover the electrode surface. Figure 3 is the CV curve for an electrode prepared in this manner. The CV curves for methyl viologen in solution or immobilized on Nafion are essentially identical.

The presence of oxidation and reduction peaks indicates that the material being tested is electrochemically active and that the material as used in the experiment is capable of electron transfer to the electrode metal, and can exchange ions with the electrolyte. When the electrode with Nafion/methyl viologen coating was cycled at various rates, the total change under each peak was essentially constant, indicating that the viologen was indeed immobilized on the electrode surface. For the purpose of this investigation, the major importance of the cyclic voltammetric curve is to show that the redox couple is active when immobilized on the metal surface and that the oxidized form is stable in a aqueous environment prior to its reduction at the instant cadmium plating is started.

Octylviologen solutions cannot be premixed with Nafion since a precipitate forms immediately. Mixing the solutions on the electrode surface also fails to give an active electrode as does absorption of octylviologen from solution into a preformed Nafion film. We were not able to immobilize the octylviologen in an acceptable manner for this study.

Anthraquinone-2-sulfonic acid (sodium salt) is an anionic material, so that immobilization requires a anionic ion exchange film.

For this purpose we synthesized a quaternarized polyvinyl pyridine using a straight chain C_8 alkyl bromide. The resulting polymeric quarternary ammonium bromide ("Q_8") was soluble in ethanol but not in water. The anathraquinone sulfonate was immobilized by absorbing it into a film of Q_8 which had been painted onto the electrode surface. The estimated weight of film plus quinone was 0.2 mg/cm^2.

Prussian blue films were prepared electrochemically on a variety of substrates. No immobilizing agent was required. The Prussian blue films prepared on passive substrates, such as stainless steel or platinum, showed good stability. All Prussian blue films prepared on carbon steel were highly unstable. Most attempts to prepare Prussian blue films on mild steel resulted in severe corrosion of the steel. We were successful in preparing Prussian blue on mild steel by galvanostatic reduction in a solution of ferric ion and potassium ferricyanide. Attempts to cycle electrodes prepared in this manner resulted in rapid potential oscillations during the reduction cycle and loss of electrochemical activity after only a few cycles. While extended cycle life would not necessarily be required for this application, limited cycle life is a sign of poor stability of the electrochemical contact between the metal and coating. Because of this instability, no Prussian blue coated membranes were tested for their effect on the hydrogen absorption behavior of steel.

3.2   Initial Plating Experiments

An initial set of experiments was run in order to test equipment and operating procedures. Recordings were made of hydrogen oxidation transients resulting from short (1 to 200 second) hydrogen generation pulses using 5 percent w/v NaF electrolyte, or resulting from short time cadmium plating. Some typical results are shown in Figure 7.
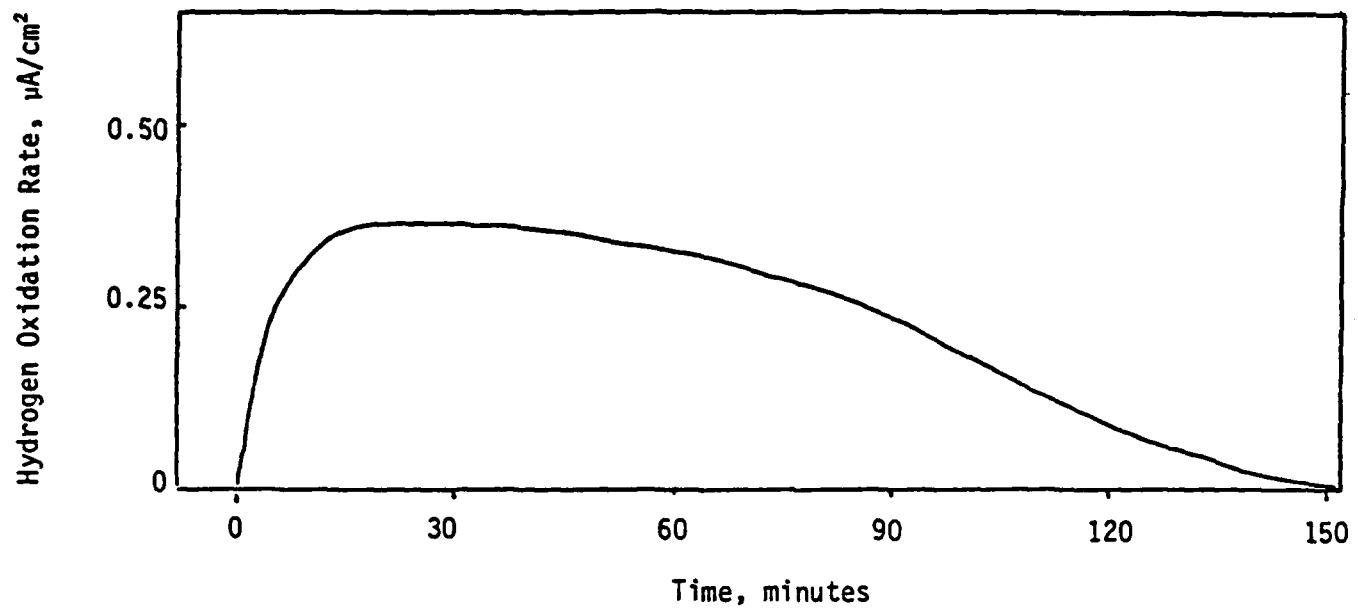
Cadmium plate; 1 second at 21 mA/cm²
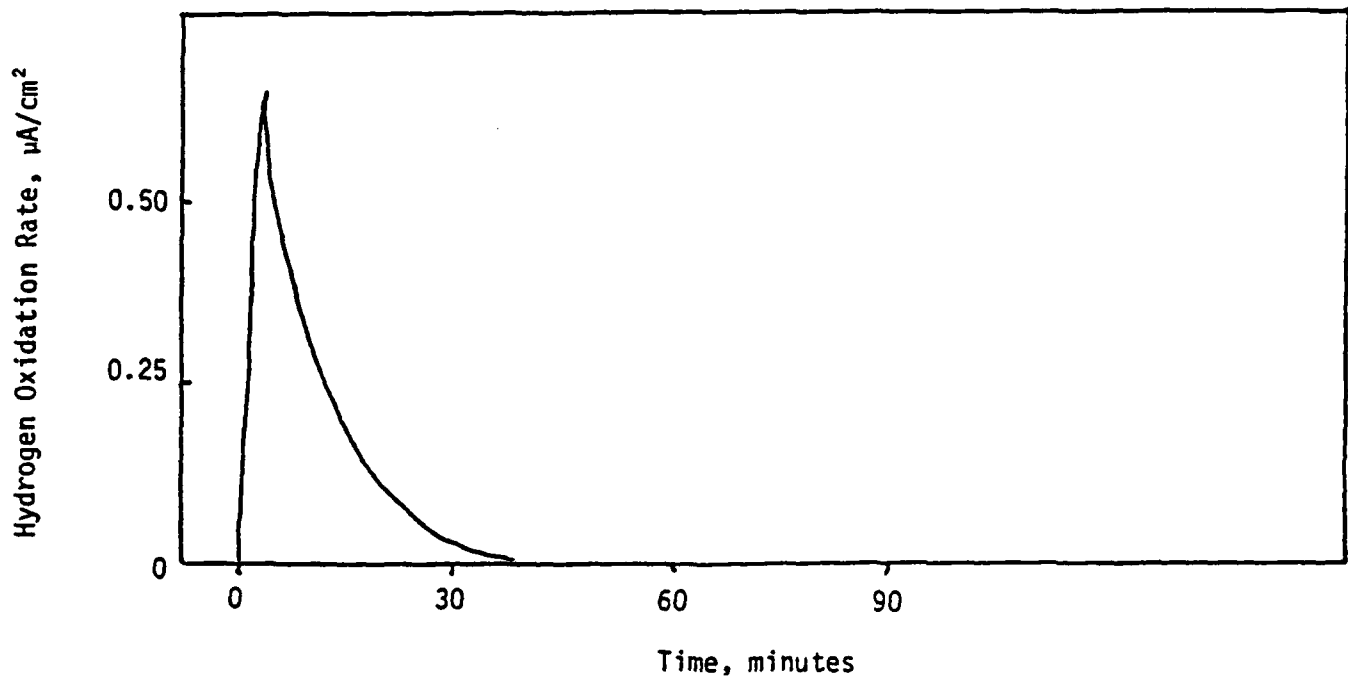
Hydrogen Generation; 100 seconds at 5 mA/cm², 5% w/v NaF electrolyte

Figure 7. Hydrogen permeation transients

3-8

The decay time of the hydrogen oxidation transient after gen-
erating hydrogen from NaF electrolyte is about 360 seconds. This is
longer than might be expected due to the fact that surface effects
predominate over bulk diffusion in the thin (0.005 cm) membrane used.
The hydrogen oxidation transients resulting from short term cadmium
plating show very long decay times and large quantities of absorbed
hydrogen (Figure 7). The integrated total hydrogen permeation through
the steel was surprisingly high. From a 430 mA sec total plating pulse
we obtained 49 mA sec of hydrogen diffusing through the steel (or about
12 percent current efficiency). Since the beginning of hydrogen diffu-
sion through the steel was delayed the expected few seconds after the
plating pulse, the hydrogen oxidation current must be the result of the
cadmium plating.

3.3   Plating on Redox Material-Coated Steel

A number of plating runs were made with uncoated steel, steel
coated only with the immobilizing ion exchange film, and with steel
coated with both ion exchange polymer and redox couple. A typical chart
of hydrogen permeation rate versus time is shown in Figure 8. Results
of all of these experiments are given in Table 1.

Each plating experiment in which the surface was modified with
an ion exchange film resulted in an increase in hydrogen absorption by
the steel during electroplating. It has been postulated that the species
discharged during electroplating from cadmicyanide solution is $Cd(OH)_2$,
an uncharged material [7]. It may be that an ion exchange film hinders
the approach of an uncharged species more than it hinders the approach
of a charged species such as hydroxyl ion, which is the ion that is most
likely reduced to yield atomic hydrogen at the metal surface. An anion
exchange film such as "Q_8" might be expected to facilitate the approach
of hydroxyl ion, and the highest hydrogen absorption rates were indeed
found when the steel surface was coated with this material.
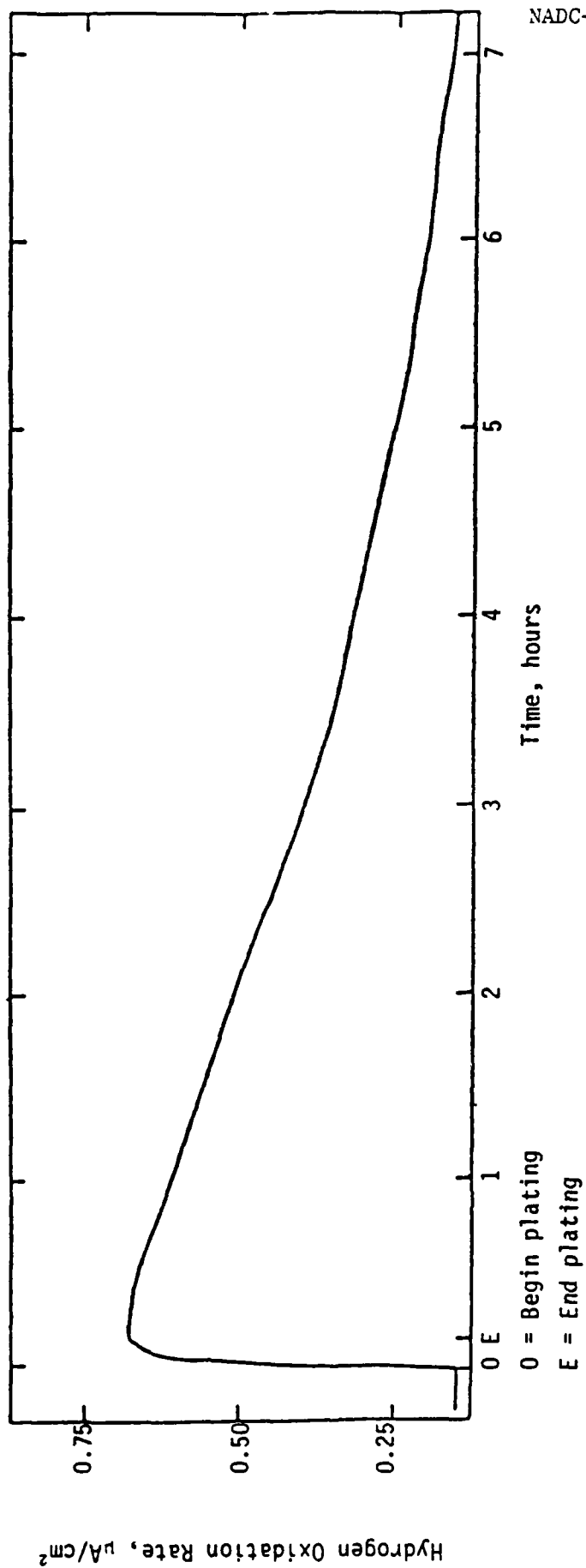
Figure 8. Hydrogen permeation after cadmium plating; Plate at 21 mA/cm² for 9 minutes, bare steel 0.005 cm thick.

O = Begin plating
E = End plating

Time, hours

Hydrogen Oxidation Rate, μA/cm²

TABLE 1

HYDROGEN DIFFUSION THROUGH STEEL RESULTING FROM CADMIUM PLATING

Plated at 21 mA/cm^2 for 550 seconds, 0.003 inch thick steel

Surface Treatment, Comments	Total Hydrogen Oxidation Charge (Millicoulombs/cm^2, 6 to 16 hours total time)
Mill finish, degreased, 4 runs	6.9 ± 1
Polished steel	10.8
Nafion coated, 3 runs	12.7 ± 1.5
Nafion/methyl viologen coated, 2 runs	16.6 ± 1
"Q$_8$" coated	33.3
"Q$_8$" + anthraquinone sulfonate	29.8
Nafion + platinum colloid	29.9
Potentiostatic plating at −1.4 V vs SCE	11.5

While the results given above may be considered as "failures," they do indicate that modification of the steel surface can influence the amount of hydrogen absorbed. For example, one might suggest that since ion exchange films increase hydrogen absorption that a nonionic film might decrease hydrogen absorption if it could selectively retard transport of hydroxyl ion or enhance transport of a species such as $Cd(OH)_2$.

A general tendency we noted in the plating experiments was that conditions which yield a visually apparent increase in roughness also lead to an increase in total hydrogen absorbed. This then produces a slower rate of diffusion of hydrogen into the steel membrane. These effects are probably due to the surface topology of the rough plate which would have greater surface area to absorb hydrogen and which would present some of the absorbed hydrogen with a much longer diffusion path in the cadmium. This tendency may explain the failure of the cationic Nafion film to decrease hydrogen absorption as its use led to a generally rougher cadmium plate.

3.4   Other Plating Experiments

During most cadmium plating experiments a slight oscillation in plating current was noted. During one experiment we measured the potential of the steel membrane using a Luggin capillary and a SCE. The potential of the membrane was found to oscillate about once each 3 or 4 seconds between - 1.9 and - 1.4 volts vs SCE. The hydrogen evolution rate varied in accordance with the potential. The rate of oscillation varied with plating current density. The example in Figure 9 shows the initial potential oscillations recorded at 21 mA/cm² of current densities.

Since the extent of hydrogen surface coverage varies with electrode potential, it appeared reasonable to determine if plating
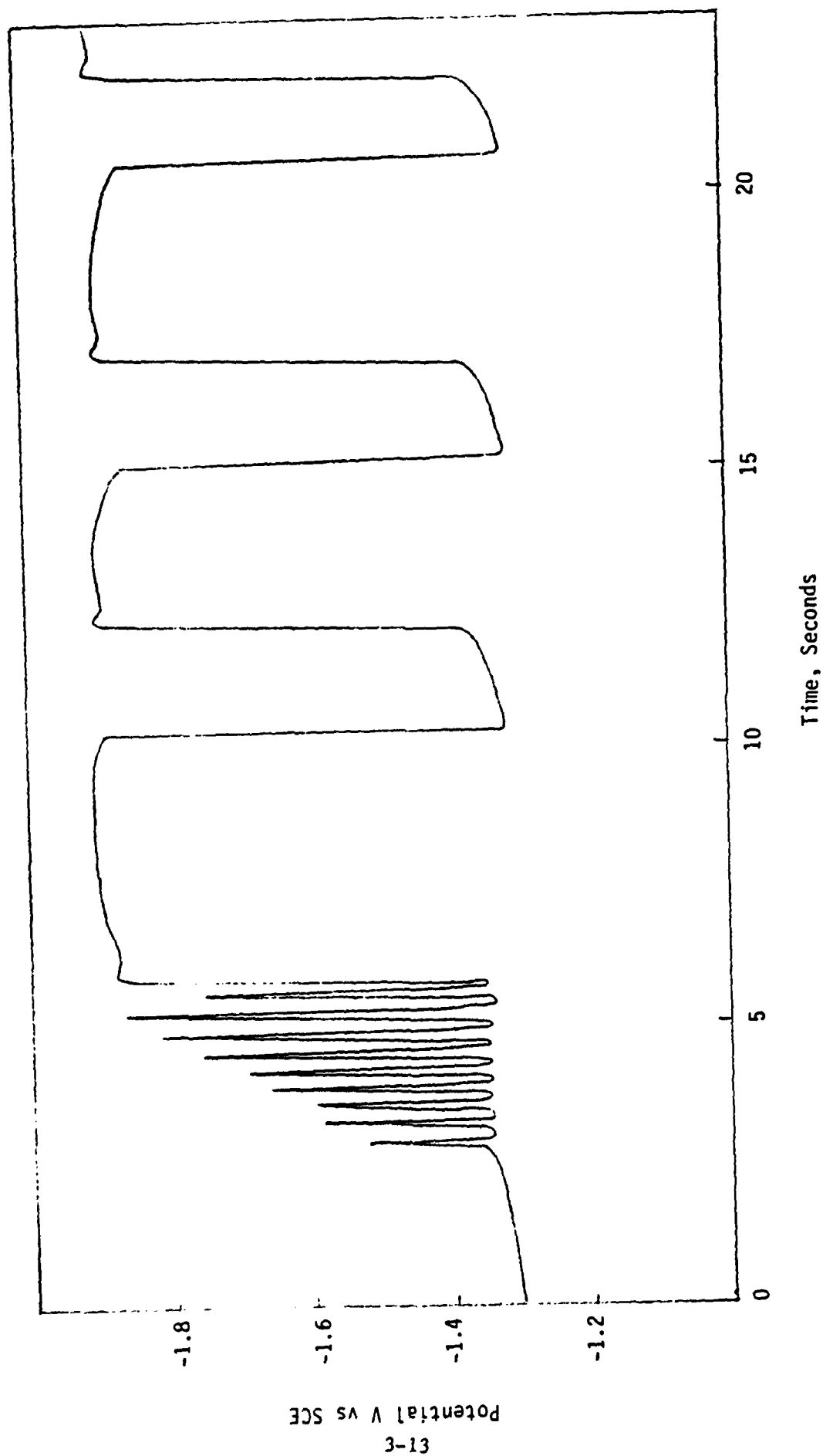
Figure 9. Potential oscillation during plating; 21 mA/cm^2

Time, Seconds

Potential V vs SCE

potentiostatically at a potential below the lower potential noted would result in decreased hydrogen absorption. However, the amount of hydrogen permeating the steel membrane appeared to be slightly higher than normal when plating was done potentiostatically at - 1.4 volts vs SCE. Thus, it appears that hydrogen coverage is essentially complete at - 1.4 volts. Results of this experiment are given in Table 1.

If it were possible to decrease the hydrogen surface coverage by promoting hydrogen evolution then the concentration of hydrogen in the cadmium plate would also decrease. One plating experiment was made in which colloidal platinum was immobilized on the steel surface with Nafion. The amount of platinum on the surface was estimated to be 0.001 mg/cm^2. The amount of hydrogen absorbed in this case was larger than that found for a Nafion coated steel sample, as shown in Table 1. By promoting the combination of hydrogen atoms to molecular hydrogen, colloidal platinum may promote additional reduction of hydroxyl ions to yield atomic hydrogen that is codeposited with cadmium, resulting in an increased concentration of hydrogen in the cadmium plate.

3.5   Barnacle Cell Plating Experiments

The barnacle cell as used by DeLuccia and Berman offers the advantage of obtaining much quicker results, perhaps with greater precision and with a much simpler mechanical arrangement. The barnacle cell measures the hydrogen in the steel as a result of plating, while the permeation cell measures the total hydrogen in both steel and cadmium plate. If the steel used in the barnacle cell experiments is thin relative to the time from start of plating until removal of the cadmium plate, then the hydrogen in the steel will be equilibrated with the hydrogen in the cadmium plate, and the results obtained by the two different techniques will agree in indicating the effect of any modification of plating procedure.

Two C1010 steel specimens 0.060 inch thick were plated to a
thickness of 0.01ᶜ mm cadmium, with or without Nafion/methyl viologen,
and with 1 percent brightener. Three hours were allowed for the
hydrogen to equilibrate the effectively 0.030 inch thick steel (both
sides plated.) The plate was stripped using ammonium nitrate (120 g/L)
and the barnacle cell was attached. Results given below show no major
effect due to the coating, in agreement with the results from the
permeation cell.

Surface Treatment	Oxidation Current at 30 min, $\mu A/cm^2$
Degreased, abraded	6.0
Plus Nafion/methyl viologen	5.5

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SECTION 4
RECOMMENDATIONS

The surface immobilized couples investigated in this study showed no evidence of decreasing the amount of hydrogen absorbed during cadmium plating. A continuation of effort on this approach to the problem does not appear to be warranted.

Two alternate approaches to the hydrogen absorption problem can be suggested. These are use of a less powerful cadmium complexing agent or the use of nonaqueous plating baths.

The solubility product constant for $Cd(OH)_2$ is approximately 7×10^{-15}. Thus the maximum free cadmium ion concentration that can exist in an alkaline medium is very low. Cadmium is complexed with cyanide ion in order to achieve the high metal concentrations required for electroplating. The strength of this complex results in an extremely low free cadmium ion concentration, which has the effect of shifting the potential required to cadmium reduction to a very negative potential, indeed to a potential considerably negative of the hydrogen evolution potential at the pH used in cadmium plating. A complexing agent that gives a less stable cadmium complex could provide a higher free cadmium ion concentration, shifting the reduction potential in a positive direction. If this potential can be shifted far enough a substantial reduction in hydrogen absorption during plating might be achieved. Complexing agents such as polyvinylpyrrolidone would be good candidates for such an investigation.

If it were possible to plate cadmium successfully from a non-aqueous solvent, it could allow plating without any hydrogen generation or absorption thus yielding a complete solution to the embrittlement problem. A substantial amount of empirical investigation has been carried out in nonaqueous media. While this should be carefully reviewed,

a more fundamental approach could offer better long-range chances for success.

In order for either approach to be successful, conditions must be found which not only result in low hydrogen absorption, but also in physically acceptable, adherent electrodeposits. The methods must also be adaptable to easily controlled, moderately large scale applications. This increases the need for long term directed research, in view of the relatively limited present fundamental knowledge of electrodeposition processes for metals such as cadmium.

Another solution to the problem would be to identify alternate corrosion protection methods for key structural parts which did not involve cadmium plating or other treatment methods which lead to hydrogen embrittlement. Electroactive coatings similar to those used in the present study could conceivably be used for such an application. Considerable optimization and environmental testing would be required to establish the feasibility of this approach.

SECTION 5

REFERENCES

1. D. W. DeBerry and A. Viehbeck, "Properties of Active/Passive Metals Modified by Electroactive Coatings" in "Fundamental Aspects of Corrosion Protection by Surface Modification," E. McCafferty, et -al, editors, Proceedings Volume 84-3, The Electrochemical Society, Inc., 1984, p. 308.

2. M. A. V. Davanathan and Z. Stachurski, J. Electrochem Soc., 111, 619 (1964).

3. J. J. DeLuccia and D. A. Berman, "An Electrochemical Technique to Measure Diffusible Hydrogen in Metals (Barnacle Electrode)" in "Electrochemical Corrosion Testing, ASTM STP 727," F. Mansfeld and U. Bertocci, editors, ASTM, 1981 p. 256.

4. N. Menschutkin, Z. Physik Chemie, 5, 589 (1890).

5. H. Braun, W. Storck and K. Doblhofer, "Thermodynamic Aspects of Redox Reactions on Electrodes Coated with Thin, Ion Exchanging Polymer Films," J. Electrochem. Soc., 130, 807 (1983).

6. H. Hirai, Y. Nakao and N. Toshima, J. Macromol, Sci.-Chem., A 13(6), 727 (1979).

7. R. J. Latham and N. A. Hampson, "Cadmium" in "Encyclopedia of Electrochemistry of the Elements, Volume 1," A. J. Bard, editor, Marcel Dekker, 1973, p. 209.

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